

1 JCO7 Rec'd PCT/PTO 29 JAN 2001

1
2
3
4
5
6
7
8
9
10
11
12
13**DISPLAYS**

14 This invention relates to display and illumination technology.

15

16 The present invention describes a method in which polymers doped with
17 fluorescent dyes can be used to fabricate display elements and illumination systems
18 for use in applications such as road signs, advertisement displays, toys etc whereby
19 the use of external electrical power is not required. The fluorescent dyes with
20 which these polymers are doped, absorb ambient light, before emitting light which
21 is conducted by the polymer host material to the end of the fibre where the emitted
22 light is of a much greater light power density than the light power density of the
23 ambient light.

24

25 In this field it is already known that flat panel display elements composed out of
26 plastic polymers can be used as display articles and that optical fibres can be used
27 to convey information in telecommunication or in display technology.

28

29 Previous application involving such materials had the disadvantage that the sign or
30 display element required illumination through the means of applying an external

1 electrical power supply with this electrical power requiring conversion into light
2 power and consequently this method consumes electrical power. Similarly, in the
3 case of optical fibres, a light source had to be located at one end of the fibre to
4 allow transmission and emission of light at the other end of the fibre.

5
6 The optical power density from the fluorescent polymer is higher than the optical
7 power of the ambient light. The ratio between these optical power densities does
8 not depend on the ambient light conditions as long as they are sufficient for
9 excitation of the fluorescent dye.

10
11 The suggested new technology does not require any external electrical power
12 because it is extracting light power directly from ambient light (sunlight or
13 artificial light).

14
15 The suggested new technology is inherently safer compared to conventional
16 electrical power based technologies it does not use any external or internal voltages
17 and/or currents for its operation.

18
19 Another advantage of using the suggested new technology is associated with the
20 fact that it does not require maintenance since it does not use electrical cables.

21
22 Further advantages include the technology used in this invention being simple,
23 environmentally friendly, having a one hundred percent recycling capacity and not
24 using the Earth's resources.

25
26 Fluorescent dye doped polymers are used to collect ambient light through the
27 introduction of red, green and blue light emitting fluorescent dyes into a polymer
28 host material. The colour of the emitted light can be changed into a required
29 specification through variation of the dyes incorporated into the polymer.

30
31 In the case of the polymer taking the form of an optical fibre, through a suitable

1 combination of optical fibre geometry and (length and diameter) and the
2 incorporation of an appropriate fluorescent dye, the light power density at the end
3 of the fibre (light emitter) can be made much larger than the light power density of
4 the ambient light and therefore can be used for illumination or display applications.
5 Furthermore, the contrast between the light power density at the end of the fibre
6 and the light power density of the ambient light remains constant because this
7 parameter only depends on the geometrical and material parameters for a given
8 polymer, but does not depend on the ambient light conditions. The end of the
9 fibres can be used as light emitting pixels in an array. By modulating the light
10 intensity at the end of each fibre selectively, the fibre array can be used as a display
11 device.

12
13 The principle of operation is shown in Figure 1 wherein an optical fibre polymer is
14 shown to be doped with fluorescent dye molecules. Similarly, a transparent
15 polymer film or sheet could also be chemically doped or blended with a fluorescent
16 dye. The fluorescent dye should have a high quantum efficiency for converting
17 natural light or indoor light into some visible colour.

18
19 It is an object of this present invention to provide a transparent polymer which can
20 be formed into a film, a sheet, an optical fibre, or similar for use in illumination
21 and display applications.

22
23 According to the present invention there is provided an optically transparent
24 polymer, such as an optical fibre, a film or sheet which is doped or blended with
25 organic fluorescent dye molecules for use in visual display wherein fluorescent
26 light is generated when artificial ambient light, daylight or sunlight enters the
27 doped polymer or optical fibres.

28
29 Whereas in general any transparent polymer may be used, suitably the transparent
30 polymer is chosen from the group comprising PMMA, polycarbonate and
31 polystyrene.

1

2 Whereas in general any organic fluorescent dye can be used, suitably the
3 fluorescent dye molecules are chosen from the group comprising PBD, Bis-MSB,
4 3-3'-diethyloxycarbocyanine-iodide and cresyl violet 670 perchlorate.

5

6 Preferably where the polymer constitutes an optical fibre, the preferred
7 embodiment of the radius of such a fibre is between 0.25 and 0.70×10^{-2} meters
8 and the length of the fibre is between 0.2 and 1.6 meters.

9

10 Where the preferred embodiment of this invention is an optical fibre, the
11 magnitude of the fluorescent light emitted from such a fibre is given by the
12 equation $A_a/A_e = 2L/r$ wherein A_a is the surface area of the fibre and A_e is the area
13 at which the fluorescent light is emitted.

14

15 Although a preferred dimension for the radius of an optical fibre embodiment is
16 given, clearly the dimensions of the fibres will depend on their use in proposed
17 displays.

18

19 The invention also provides the use of the fibres as display pixels where artificial
20 ambient light or sunlight provides excitation sources.

21

22 The invention further provides display devices comprising a plurality of fibres as
23 described herein.

24

25 The plurality of fibres may include fibres to emit a variety of colours.

26

27 The devices may further comprise shutters to control emission from the individual
28 fibres in a device.

29

30 Preferably where there exists a flat panel display or sheet embodiment of this
31 invention, the bottom surfaces and edges of the polymer film are covered with a

1 highly reflective additional layer which acts as a mirror performing the role of total
2 internal reflection of all light entering into the polymer.

3

4 Preferably also in such embodiments, the top surface of the polymer shall be
5 covered with a dielectric stack mirror. In a preferred embodiment of this stack it is
6 constituted of an alternating sequence of two dielectric films with alternately high
7 and low refractive indices.

8

9 The composition of this dielectric stack is such that the aforementioned stack shall
10 act as an interference filter to allow nearly 100% transmission of light from air into
11 the polymer for wavelengths used for excitation of the dye. Further this
12 aforementioned stack has nearly 100% reflection for light wavelengths emitted
13 from the fluorescent dyes. The dielectric layers can be vacuum evaporated, spin
14 coated or sputtered onto the surface of the polymer.

15

16 In an alternative preferred embodiment of this dielectric stack, thin films of two
17 different polymers, with the two different refractive indices, can be applied to the
18 polymer surface sequentially and vacuum pressed and/or thermally treated for each
19 layer. This method has the advantage that it allows larger areas to be covered by
20 the dielectric stack mirror.

21

22 Alternatively, cladding can also be used for the same purpose although the
23 efficiency is not as good as with the dielectric stack mirror.

24

25 The present invention can be adapted for display purposes as the fluorescent light
26 emitted from the dye can be coupled out from the polymer at the top surface by
27 emitting or removing the dielectric stack mirror at a given surface area and by
28 making an uneven or grating surface at the polymer air interface. The grating
29 structure should be maximised for maximum diffraction for the emitted fluorescent
30 light wavelength.

31

1 In an alternative preferred embodiment of this form of the invention, the
2 replacement of the bottom mirror layer of the dielectric stack mirror, identical to
3 the one applied to the top surface allows a combined reflective and transmissive
4 mode of light collection and display operation.

5
6 Further an alternative preferred embodiment of the invention provides a further
7 combination of dielectric stack and mirror combinations while using the principles
8 previously described. In this embodiment the dielectric stack mirror is applied on
9 both sides of the transparent polymer-dye matrix but no side mirrors are applied.
10 Consequently the fluorescent light generated inside the polymer will be
11 waveguided towards the edges of the polymer.

12 The invention also provides methods for producing displays as set out herein.

13

14 The invention will now be described with reference to the accompanying figures
15 wherein:

16

17 Figure 1 describes the principles of Fluorescent Dye Doped Optical

18

19 Figure 2 shows Absorption-Emission spectra of Nile Red in Polystyrene

20

21 Figure 3 shows Absorption-Emission spectra of Coumarin 6 in Polystyrene

22

23 Figure 4 shows Absorption-Emission spectra of BisMSB in Polystyrene

24

25 Figure 5 shows NR 0.04 wt% + C6 in Polystyrene vs. wavelength.

26

27 Figure 6 illustrates Nile Red + Coumarine 6 in Polystyrene.

28

29 Figure 7 illustrates Absorption - Emission Area of Nile Red 0.04 % + Coumarine 6
30 + Bis MSB.

31

- 1 Figure 8 illustrates Quantum Yield of Coumarin 6 in polystyrene.
2
3 Figure 9 shows Absorption - Emission Area of Coumarin 6 in Polystyrene.
4
5 Figure 10 shows Quantum Yield of Bis MSB in Polystyrene.
6
7 Figure 11 illustrates Arrangement for light scattering/Absorption measurements.
8
9 Figure 12 describes Scattered light intensity from polycarbonate red and green
10 fibres.
11
12 Figure 13 demonstrates Polycarbonate Fibres/ Polycarbonate with red/green laser
13
14 Figure 14 demonstrates Intensity of green/red fibre in sunlight while fibres are
15 partially covered (normalised and an average of 7 measurements/ y-errors equal 2
16 sigma.
17
18 Figure 15 shows Structure of Light Emitting Polymer in combined reflective and
19 transmissive mode.
20
21 Figure 16 shows the structure of Light Emitting Polymer in the Edge emitting.
22
23 Figure 17 demonstrates Green Reflectance.
24
25 Figure 18 demonstrates GREEN1 Transmittance.
26
27 Figure 19 demonstrates RED1 Reflectance
28
29 Figure 20 demonstrates RED1 Transmittance
30

1 Figure 21 shows a display in full sunlight conditions.

2

3 Figure 22 shows a display in cloudy conditions

4

5 Figure 23 shows a display in late evening condition (two hours after sunset).

6

7 Detailed Description of Figures

8

9 **Figure 1: Fluorescent Dye Doped Optical Waveguide;** describes the principle of
10 operation for the fluorescent dye doped polymer optical fibre. The principle steps
11 of operation are as follows:

12

13 1) Ambient light is absorbed by fluorescent dye,

14 2) Dye re-emits fluorescent light

15 3) Fluorescent light is waveguided if angle of incidence $\gamma \geq \theta_c$ where $\theta_c =$
16 critical angle for total internal reflection

17 4) Fluorescent light is leaked out of the waveguide if $\gamma < \theta_c$

18

19 The intensity of the fluorescent light at the end of the optical-waveguide depends
20 on the following physical parameters;

21

22 Ambient light intensity

23 Overlap of the spectral distribution of the ambient light and the light absorption of
24 the fluorescent dye

25 Absorption coefficient of the dye in the light absorption region

26 Absorption coefficient of the polymer core and polymer cladding in the light
27 absorption region

28 Absorption coefficient of the polymer core and polymer cladding in the fluorescent
29 light emission region

30 Refractive index of the polymer core

31 Refractive index of the polymer cladding

- 1 Optical uniformity of the core (scattering)
- 2 Optical uniformity of the cladding (scattering)
- 3 Geometry of the optical waveguide structure
- 4
- 5 Optimisation of these parameters results in an optical power flux emitted at a
- 6 selected spectrum of wavelengths from the end of the waveguide at an increased
- 7 flux than the flux of the ambient light i.e. optical amplification is obtained.

8

9

10 **Figure 2: Absorption-Emission spectra of Nile Red in Polystyrene;** shows the

11 absorption (excitation) and emission spectra of polystyrene polymer doped with

12 0.01, 0.02 and 0.05 wt% of Nile Red fluorescent dye. The dye absorbs the ambient

13 light in the wavelength region from ~ 300 nm to ~ 570 nm and re-emits the light in

14 the wavelength region from $\lambda \sim 570$ nm to $\lambda \sim 670$ nm. The maximum intensity of the

15 fluorescent light occurs at $\lambda_{\text{max}} = 602$ nm i.e. the polymer emits red light.

16

17 **Figure 3: Absorption-Emission spectra of Coumarin 6 in Polystyrene;** shows

18 the absorption and emission spectra of polystyrene polymer doped with 0.07, 0.09

19 and 0.15 wt% of Coumarin fluorescent dye. The dye absorbs the ambient light in

20 the wavelength region from $\lambda \sim 250$ nm to $\lambda \sim 510$ nm and re-emits the

21 fluorescent light in the wavelength region from $\lambda \sim 510$ nm to $\lambda \sim 560$ nm. The

22 maximum intensity for the fluorescent light occurs at $\lambda_{\text{max}} = 522$ nm i.e. the

23 polymer emits green light.

24

25 **Figure 4: Absorption-Emission spectra of BisMSB in Polystyrene;** shows the

26 absorption and emission spectra of polystyrene polymer doped with 0.02 and 0.04

27 wt% of Bis MSB fluorescent dye. The dye absorbs the ambient light in the

28 wavelength region from $\lambda \sim 250$ nm to $\lambda \sim 410$ nm and re-emits the fluorescent

29 light in the wavelength region from $\lambda \sim 410$ nm to $\lambda \sim 470$ nm. The maximum

30 intensity for the fluorescent light occurs at $\lambda_{\text{max}} = 430$ nm i.e. the polymer emits

31 blue light.

1
2 **Figure 5: NR 0.04 wt% + C6 in Polystyrene vs. wavelength;** shows the
3 absorption and emission spectra of polystyrene polymer doped simultaneously with
4 two fluorescent dye, Nile Red and Coumarin 6 respectively. Figure 5 is also an
5 example of increasing the efficiency of red fluorescent light emission by using
6 larger concentration of Coumarin 6 in the two component dye mixture. The relative
7 efficiency for light generation increases by a factor of 2.4 when the Coumarine 6
8 dye concentration increases from 0.01 wt % to 0.04 wt % in the dye mixture.
9 Figure 5 also shows that this increase in the efficiency is due to two factors; firstly
10 due to increased absorption and secondly due to increased energy transfer of green
11 light emission to red light emission.

12
13 **Figure 6: Nile Red + Coumarine 6 in Polystyrene;** summarises the relative
14 efficiencies of ambient light absorption and fluorescent light emission as a function
15 of the concentration of the dyes in the two component dye mixture in polystyrene
16 host polymer. The largest efficiency for absorption and fluorescent light emission
17 is obtained at 0.02 wt % of Coumarine 6 combined with 0.03 wt% Nile Red.

18
19 **Figure 7: Absorption - Emission Area of Nile Red 0.04 % + Coumarine 6 + Bis**
20 **MSB;** describes the relative efficiencies for fluorescent light emission in a three
21 component dye mixture in the polystyrene polymer host. The largest efficiency is
22 obtained at the composition of 0.02 wt% Nile Red + 0.03 wt% Coumarin 6 + 0.01
23 wt % Bis MSB. Either increasing or decreasing the concentration of Bis MSB will
24 result in a drop in efficiency for light generation.

25
26 **Figure 8: Quantum Yield of Coumarin 6 in polystyrene;** describes the quantum
27 Yield of coumarin 6 in polystyrene as a function of dye concentration. The
28 optimum efficiency is obtained at 0.06 wt %.

29
30 **Figure 9: Absorption - Emission Area of Coumarin 6 in Polystyrene;** describes
31 the relative magnitudes of absorption and fluorescent light emission as a function

1 of dye concentration. The comparison of Figure 8 and Figure 9 shows that the
2 maximum efficiency for fluorescent light generation (at 0.06 wt%) is according to
3 the maximum in the quantum yield (at 0.06wt%). Figure 9 also shows that the
4 maximum in absorption is not necessarily according to the
5 maximum in light emission.

6

7 **Figure 10: Quantum Yield of Bis MSB in Polystyrene;** describes the quantum
8 yield of blue light generation as a function of dye concentration.
9 The best efficiency is obtained at 0.035 wt %.

10

11 **Figure 11. Arrangement for light scattering/Absorption measurements;** this
12 provides data for combined scattering and absorption profile within the fibre
13 because the optical losses are due to two factors; a) absorption b) scattering.

14

15 **Figure 12: Scattered light intensity from polycarbonate red and green fibers;**
16 describes the combined scattering / absorption data for fluorescent dye doped red
17 and green polycarbonate (dye) optical fibres.

18

19 The ♦*■ symbols refer to scattering / absorption data on polycarbonate fibres
20 doped with increasing concentration of Coumarine 6 dye. These measurements are
21 obtained by using an Ar ion laser ($\lambda = 513$ nm). The ^ • ○ symbols refer to
22 scattering/absorption data on polycarbonate fibres doped with increasing
23 concentration of Nile Red dye. These measurements are obtained by using a He-Ne
24 laser ($\lambda = 632$ nm).

25

26 All of the curves show the scattered light intensity as a function of the length l from
27 the end of the fibre. The plots are linear in the semilogarithmic scale thus
28 confirming the exponential nature of the light decay along the fibre. Generally the
29 Red fibres (Nile Red NR doped polycarbonate) have more loss (measured at λ
30 $= 632$ nm) than the Green fibres (Coumarine 6, C6 doped polycarbonate), measured
31 at $\lambda = 513$ nm. This is due to the dispersion of the refractive index (the refractive

1 index is smaller in the red spectral region than in the green spectral region). Figure
2 12 also shows the effect of the increase of the dye concentration on the
3 scattering/absorption properties. As a particular dye concentration (Nile Red or
4 Coumarine 6) increases, the scattering/absorption losses decrease (slope is
5 becoming less) This is demonstrated by comparing the concentration of NR at 0.01
6 wt% and 0.03 wt %, and the comparison of C6 at at 0.01 wt% and 0.05 wt %
7 respectively. The increased efficiency for fluorescent light collection therefore is
8 due to the combined effect of increasing the dye concentration and the increase in
9 the refractive index of the polymer (dye) guest host core.

10

11 **Figure 13: Polycarbonate Fibres/ Polycarbonate with red/green laser;**
12 demonstrates the increase of the refractive index of the polycarbonate/C6
13 polymer/dye guest host system as a function of the C6 dye concentration. There is a
14 linear dependence of the refractive index from $n = 1.555$ to $n=1.585$ on the dye
15 concentration in the range between 0.035 wt% and 0.065 wt%.

16

17 **Figure 14: Intensity of green/red fibre in sunlight while fibres are partially**
18 **covered (normalised and an average of 7 measurements/ y-errors equal 2**
19 **sigma);** demonstrates that the fluorescent light generation under sunlight excitation
20 is saturated after ~ 60 cm length of the fibre. This is because the extra light
21 generated in the middle of the fibre is scattered out or absorbed within the core.
22 Comparison of Figure 14 with Figure 13, shows a good agreement, confirming the
23 nature of light losses.

24

25 **Figure 15: Structure of Light Emitting Polymer in combined reflective and**
26 **transmissive mode;** shows the structure of a polymer and the positioning of a
27 dielectric stack relative to it.

28

29 **Figure 16: Structure of Light Emitting Polymer in the Edge emitting Mode;**
30 shows the dielectric stack use in relation to an optical fibre polymer, where the
31 dielectric stack mirror provides a band pass antireflection - reflection layer which

1 acts as an absorption free band pass filter for transmitting all of the spectral region
2 of the ambient light for excitation of the fluorescent dye but reflects all of the
3 emitted fluorescent light back to the sample.

4
5 **Figure 17: GREEN Reflectance;** demonstrates the Reflectance spectrum of the
6 dielectric stack described in Table II.. The reflectance is nearly zero in the
7 wavelength region from ~ 350 nm to 430 nm. This means that this spectral region
8 of ambient light can be used for excitation of Coumarine 6. Comparison of Figure
9 17 with Figure 3. shows that the zero reflection region corresponds to the spectral
10 region of absorption (excitation) region (~ 350 nm to 480 nm) for Coumarine 6).
11 Alternatively, the reflectance is nearly 100 % for the spectral region from 450 nm
12 to 550 nm. Comparison of Figure 14 with Figure 3 shows that the high reflectance
13 region corresponds to the spectral region of green fluorescent light emitted by C6.
14 This means that the emitted light is fully reflected back to the bulk of the flat panel.

15

16

17 **Figure 18: GREEN1 Transmittance;** demonstrates the Transmittance spectrum
18 of the same dielectric stack as described in Table II. The Transmittance is ~ 80 %
19 in the spectral region from ~ 350 nm to 430 nm. This allows the light to be
20 transmitted for excitation. On the other hand, the transmittance is nearly zero in the
21 spectral region from 450 nm to 550 nm. Comparison of Figure 18 with Figure 3
22 shows that the zero transmittance region corresponds to the spectral region of green
23 fluorescent light emitted by C6. The panel looks deep blue in appearance as it
24 transmits only blue light in the visible region, therefore, the contrast between the
25 uncovered (bright green) and dielectric stack covered (dark blue) areas of the flat
26 panel can be substantial, which is suited for display applications.

27

28 **Figure 19: RED1 Reflectance;** demonstrates the reflectance spectrum of a
29 dielectric stack for a dielectric stack mirror designed with specification detailed in
30 Table III. The reflectance has a nearly zero value in the spectral region from ~ 350
31 nm to ~ 500 nm. Comparison of Figure 19 with Figure 2 shows that the zero

1 reflectance region corresponds to the absorption region of the Nile Red dye in
2 Polystyrene. Alternatively, nearly 100 % reflectance region (~ 530 nm to 650 nm)
3 corresponds to the light emission spectral region of the Nile Red in Polystyrene.

4

5 **Figure 20: RED1 Transmittance;** demonstrates the transmittance spectrum of
6 the same dielectric stack as described in Table III. Comparison of Figure 20 with
7 Figure 2. confirms that the high transmittance region corresponds to the spectral
8 region of Nile Red absorption in Polystyrene.

9

10 **Figures 21, 22 and 23 show a constant contrast of fluorescent polymer based**
11 **display;** where Figure 21 shows the display in full sunlight conditions, Figure 22
12 shows the display in cloudy conditions and Figure 23 shows the display in late
13 evening condition (two hours after sunset). The photographs shown in figures 20,
14 21 and 22 demonstrate the concept of "constant contrast" between the light emitted
15 from the end of the fibres and the intensity of the ambient light.

16

17 It is already stated earlier that the contrast between the light power flux emitted
18 from the end of the fibre and the ambient light power flux is constant because this
19 property does not depend on the ambient light intensity. The photos clearly show
20 that the contrast between the "NAPIER" sign, the blue line above the Napier sign
21 and the ambient light intensity remains fairly constant down to very low level of
22 illumination (2 hours after sunset).

23

24 Additionally, any transparent polymer can be used as core and/or cladding material.
25 In practice the choice is limited by the compatibility of the polymer core with the
26 fluorescent dye and the requirement for employing high refractive index material
27 for the polymer core and low refractive index material for the polymer cladding.
28 Polymers are favoured over glasses for several reasons such as low temperature
29 processing capability (for fibres and polymer mouldings), compatibility with
30 organic fluorescent dyes and good mechanical properties (strength and flexibility).

31

1 In principle, any fluorescent dye compatible with any transparent polymer can be
2 used for this purpose. In practice the choice is limited by the compatibility of the
3 fluorescent dye with the polymer core, the required colour, and the stability and
4 lifetime. The contrast between the light power density emitted from the polymer
5 and the light power density of the ambient light remains constant because this
6 parameter is not effected by ambient light conditions as long as they are above a
7 critical level and instead relies on the material parameters.

8

9 Typical examples for the core are; polymethylmethacrylate (PMMA), polystyrene,
10 polycarbonate, cyclic olefin copolymers, or any similar transparent polymer,
11 commercially available as either monomers or polymers from Aldrich, BASF,
12 Bayer, GE Plastics, Ticona or other suppliers.

13

14 Typical examples for the fluorescent dye are; Coumarin 6 (green fluorescent dye),
15 Coumarin 7 (green fluorescent dye), Coumarine 314 (green fluorescent dye) 1,8-
16 Diphenyl-1,3,5,7, - octatetrene (yellow fluorescent dye) Nile Red (red fluorescent
17 dye), Bis-MSB (blue fluorescent dye), Cresyl Violet Perchlorate (red fluorescent
18 dye), Sulforhodamine 101 (red fluorescent dye), Sulforhodamine 640 (red
19 fluorescent dye), commercially available from Aldrich or Exciton, or other
20 suppliers.

21

22 The fluorescent dyes can be incorporated into the core polymers by any suitable
23 method, including:

- 24 1. Dissolving the dyes in the monomer and then carrying out bulk polymerisation
25 to produce a cast sheet or rod preform (for fibre drawing).
- 26 2. Melt compounding of dyes into polymer using either a batch internal mixer, or
27 continuous compounding equipment (such a single screw extruder or a twin
28 screw extruder).

29

30 Typical initiators such as AIBN and Benzoyl Peroxide are also available
31 commercially from Aldrich or other suppliers.

1

2 **Method of polymerisation:**

3

4 Polymerisation is carried out directly from the monomer (with dye dissolved in it)
5 or more often from a monomer-polymer syrup approximately 20-40 weight percent
6 of polymer. Prior to polymerisation, the fluorescent dye is dissolved in the
7 monomer. This is a preferred method for dissolution because of the simplicity of
8 the process and because there is no need to apply an extra solvent which would
9 decrease the efficiency of the dye in the host matrix.

10

11 The fluorescent dye concentration in the monomer is in the range of 0.005 weight
12 % to 0.2 weight %. The polymerisation is carried out in the temperature range from
13 20°C to 50°C in steps over 5 hours and keeping the material for 12 hours at 50°C.

14 The slow process helps control the exotherm effect during polymerisation. If the
15 material is overheated during the polymerisation, volatile monomer can produce
16 bubbles inside the material resulting in defects and optical non-uniformities within
17 the final polymer product. Therefore it is important to control the polymerisation
18 temperature range. Alternatively other polymerisation techniques may be used, for
19 example using ultra-violet light. By such a method rods can be cast in glass tubes
20 to produce polymer (dye) rods approximately 25 mm in diameter and 1 metre in
21 length suitable for drawing into optical fibres.

22

23 Optical fibre drawing of the rods can be based on the rod in tube method using a
24 process similar to that used for glass optical fibre (though at a very much lower
25 temperature). In the preferred embodiment a polystyrene (Coumarin 6) rod is
26 placed inside a PMMA tube. The rod in tube structure is surrounded by an oven
27 which has a temperature around 265°C. The oven heats up the rod in tube structure
28 and consequently the viscosity of both the rod and the tube decreases to a value
29 close to that of the liquid phase. Simultaneously, with the heating, a tension is
30 applied via a wheel and belt system to the rod in tube structure. The combined
31 effect of temperature and tension results in fibres drawn from the rod in tube. The

1 internal core is drawn from the rod and the outer cladding is drawn from the tube.
2 Polystyrene has a higher refractive index so it is used as the core material and
3 polymethylmethacrylate has a lower refractive index so it is used as the cladding
4 material.

5
6 Other techniques can also be used to produce the polymer (dye) -polymer, core-
7 clad fibre, such as continuous extrusion. The core is extruded and the cladding
8 applied by: coextrusion at the die-head; downline by crosshead die extrusion
9 (similar to that used for wire covering); or solution coating.

10 A typical example of co-extruded fibre is polycarbonate core with fluoropolymer
11 cladding, but the same method can be used for polystyrene fibres clad with
12 polymethylmethacrylate.

13
14 In general a polycarbonate (dye) core with a suitable low refractive index
15 fluoropolymer such as FEP or amorphous Teflon, (both produced by DuPont) for
16 cladding can be used to make fluorescent optical fibres.

17
18 Table I illustrates several examples giving values of light power flux from optical
19 fibres at an ambient sunlight power flux of $P_s = 0.05 \text{ W/m}^2$.

20
21 **Examples:**

22
23 As a first example of the invention Figure 1 describes the structure of the light
24 emitting polymer in reflective mode. The transparent polymer is chemically doped
25 or blended with a fluorescent dye. The fluorescent dye should have a high
26 quantum efficiency for converting natural light or indoor light into some visible
27 colour. The bottom surface and edges of the polymer are covered with a highly
28 reflective additional layer which acts as a mirror and ensures that all light entering
29 through the top surface is fully reflected back into the polymer.

30
31 The top surface of the polymer is covered with a dielectric stack mirror which

1 comprises two dielectric films with alternating high and low refractive indices.
2 This dielectric stack serves as an interference filter allowing 100% transmission of
3 light from the air to the polymer for the wavelengths used for excitation of the
4 fluorescent dyes doped within the polymer. The dielectric stack however has a
5 near 100% reflection for light wavelengths emitted from the fluorescent dyes doped
6 within the polymer. The dielectric layers can be vacuum evaporated, spin coated or
7 sputtered onto the surface of the polymer.

8
9 Alternatively, thin films of two different polymers with two different refractive
10 indices can also be applied to the polymer surface sequentially vacuum pressed
11 and/or thermally treated for each layer. This method allows larger areas to be
12 covered by the dielectric stack mirror. Alternatively, cladding can also be applied
13 for the same purpose although the efficiency is not as good as with dielectric stack
14 mirror.

15
16 This arrangement, coupled with the fact that the polymer layer itself acts as a guide
17 for light generated inside the polymer (polymer refractive index about 1.5, air
18 refractive index about 1), ensures that the polymer layer acts as a "light-trap" for
19 wavelengths used for excitation and light emission from the fluorescent dye
20 embedded in the polymer matrix.

21
22 On the other hand the fluorescent light emitted from the dye can be coupled out
23 from the polymer at the top surface by emitting or removing the dielectric stack
24 mirror at a given surface area and by making an uneven or grated surface at the
25 polymer/air interface. The grating structure should be maximised for maximum
26 diffraction for the emitted fluorescent light wavelength.

27
28 The intensity of the fluorescent light I_l ($\text{mW}/\text{cm}^2/\text{nm}$) emitted from the dye doped
29 polymer (at a given dye concentration) at the grated surface is linearly proportional
30 to the R_l at a given dye concentration;

31

1 $I_1 \sim R_1 = \text{total light collecting surface area (cm}^2\text{)} / \text{total grated area (cm}^2\text{)}$

2

3 This means that the larger ratio (R_1) produces more fluorescent light. On the other
4 hand, the contrast of the display defined as the intensity of the fluorescent light
5 from the grated surface divided by the intensity of the ambient light is constant
6 because this ratio is only dependent on the geometry of the display device (at a
7 given dye concentration). This feature is particularly useful under variable ambient
8 light conditions.

9

10 The device described above can be used to display letters, characters, symbols etc
11 by using natural or artificial light from the environment and converting this light
12 into a characteristic colour of fluorescent light and directing it (by total internal
13 reflection or by interference) into the display area. By selecting the appropriate
14 dye-polymer combination and by maximising the ratio of light collecting area
15 divided by light emitting display area of a contrast of 10:1 or larger can be
16 achieved for display purposes. This contrast is independent from the ambient
17 lighting conditions. It is emphasised again that this device does not consume any
18 electrical power. However, the device will not provide enough light for the display
19 purposes when the ambient light intensity decreases below a critical level. In this
20 case a conventional light source can be switched on to provide light for excitation
21 and consequently displaying information. This electrical source does not
22 illuminate the display directly and works in an indirect fashion.

23

24 An alternative example of the invention is shown in Figure 15. By replacement of
25 the bottom mirror layer with a dielectric stack mirror, identical to the one applied
26 to the top surface, a combined reflective and transmissive mode of light collection
27 and display operation is also possible. The principle of operation is shown in
28 Figure 15. A combined reflective and transmissive mode of operation is
29 particularly useful for displays fixed on the inside of shop windows. Again as in
30 the reflective mode of operation, the contrast for displaying information is
31 independent of ambient lighting conditions.

1
2 A third mode of operation is shown in Figure 15. A dielectric stack mirror is
3 applied on both sides of the transparent polymer-dye matrix but no side mirrors are
4 applied. Consequently the fluorescent light generated inside the polymer will be
5 waveguided towards the edges. The value of fluorescent light intensity I_2
6 ($\text{mW}/\text{cm}^2/\text{nm}$) at the edges is directly proportional to the R_2 ;

7
8 $I_2 \sim R_2 = \text{total light collecting surface area (cm}^2\text{)} / \text{edge area (cm}^2\text{)} \text{ at a given}$
9 concentration of fluorescent dye.

10
11 In summary the devices described above can be used to display letters, characters,
12 symbols etc by using natural or artificial light from the environment and converting
13 this light into a characteristic colour of fluorescent light and directing it by total
14 internal reflection or by interference into the display area. Through selection of the
15 appropriate dye polymer combination and by maximising the ratio of light
16 collecting area dividing by light emitting display a contrast of 10:1 or larger can be
17 achieved for display purposes. This contrast being independent from ambient
18 lighting conditions.

19
20 The key elements of the invention are;

21
22 A method in which fluorescent dye doped polymer based optical wave-guide
23 structures such as optical fibres, arrays of fibres, woven arrays of fibres, rods,
24 sheets, folded sheets and moulded shapes of arbitrary geometry can be used to
25 fabricate display and/or illumination elements for a range of applications such as
26 road signs, traffic signs, safety signs, fixed advertisements, animation, dynamic
27 display elements, toys, games lamps etc., without the usage of external electrical
28 power thus saving energy.

29
30 A method in which display elements fabricated from fluorescent dye doped
31 polymer wave-guide structures can provide a constant contrast between the light

1 power flux emitted from the wave-guide structure and the light power flux of the
2 ambient light. This is a unique feature as compared to conventional electrically
3 powered display elements.

4
5 A method in which a dielectric stack mirror layer fabricated on the surface of flat
6 panels, sheets, and/or moulded surfaces and any other optical elements described
7 above can be used to improve the efficiency and the contrast of those optical
8 elements.

9
10 A method in which the efficiency of the fluorescent dye doped polymer based
11 optical wave-guide structures can be improved by optimising the refractive index
12 of the cladding layer.

13
14 A method in which fluorescent dye doped polymer based optical wave-guide
15 structures can provide optical amplification of the emitted fluorescent light by
16 optimising the wave-guide geometry, the composition of the dye (or dye mixtures)
17 the dye concentrations, and the polymer host.

18
19 A method in which fluorescent dye doped polymer based optical wave-guide
20 structures can provide a range of colours in the visible spectrum (from red to blue)
21 by absorbing the ambient light (artificial and/or sunlight) and converting them into
22 the required colour specification depending on the specific choice of the dye and
23 the polymer.

24
25 Methods for a range of specific applications using fluorescent dye doped optical
26 wave-guide structures which are detailed in the application section

27
28 Methods for a range of applications in which a range of specific applications using
29 fluorescent dye doped optical wave-guide structures can be combined with
30 established generic technologies.

31

1 **Applications:**

2

3 '24 hour' road signs.

4

5 An array of light-emitting rods, each one having a shuttering mechanism at its end,
6 is housed in an enclosure, along with a solar panel and battery which is used to
7 power a light during the hours of darkness. This light is activated by a light sensor
8 and provides an appropriate spectrum for energy conversion by the rods. The solar
9 panel charges the battery during the daylight hours, when the light source is not
10 required. An example of such a device and the principles involved, is shown in
11 Figure 23.

12

13 24 hour' traffic lights.

14

15 Using the fibres' qualities of producing red, green and amber fluorescent colours, a
16 system can be designed to simulate traffic lights, with the sequence control
17 circuitry, light sensor and night light powered using the solar panel / battery
18 combination (as detailed in "'24 hour' road signs' application). An example of such
19 a device and the principles involved, is shown in Figure 24.

20

21

22 **Fixed advertisements:**

23

24 These can take one of several primary forms, or combinations of these forms. The
25 first form is that of fibres / rods, as used in the '24 hour road signs, but without
26 using any shuttering process. i.e. they continuously display an unchanging image,
27 whether that image is in the form of characters, symbols, logos, or in the style of a
28 picture, or in some combination of these.

29 The lengths of fibres / rods would not be shown, only the artwork as would be seen
30 from the front is displayed.

31

1 The second form is that of a contoured sheet format, where the edges of the sheet
2 emit light and form the display; this can take the form of characters, shapes, logos.

3

4 The third format is that of a sheet which has a dielectric stack mirror coated onto
5 the surface. An example of such a device and the principles involved, is shown in
6 Figure 25. The purpose of the coating is to allow sunlight to penetrate into the
7 sheet material, and to energise the incorporated dye, but then to trap the fluorescent
8 light produced within the sheet, by reflecting these fluorescent wavelengths back
9 from the surface coating. By selectively removing parts of the coating, light is
10 permitted to escape from the sheet, and this forms the basis of a display. In this
11 way, characters, symbols, logos, diagrams etc. can be produced.

12

13 Operation of doped material during the hours of darkness can also be achieved
14 using material which can absorb light from street lights (from the sodium D lines
15 589.0 and 589.6 nm) and convert it to red fluorescent light. Typical materials,
16 along with their maximum excitation wavelength ($\lambda_{exc.max}$) and their maximum
17 emission wavelength ($\lambda_{em.max}$) are :

18

19	<u>Material</u>	<u>$\lambda_{exc.max}$</u>	<u>$\lambda_{em.max}$</u>
20	cresyl violate perchlorate	593	615
21	oxazine 4 perchlorate	610	625
22	sulforhodamine 101	578	605
23	LD 690 perchlorate	616	625

24

25 Toys.

26

27 The integration of this technology into toys can take on several forms. Fibres can
28 be transformed into flowers, where the long stem gathers the sunlight and the head
29 / petals etc. emit the fluorescent light. Doll's hair and cat's whiskers can also use
30 this approach.

31

1 Sheet format can be used to produce structures which are colourful and strong, yet
2 virtually transparent, where its edges emit fluorescent light e.g. a doll's house,
3 where the interior decoration / furniture can be viewed through the exterior walls,
4 and the light is emitted from around the windows / door / roof edges etc. to give the
5 impression of a 'magic' house.

6

7 Moulding of the material into different shapes can be done. These shapes may
8 either be hollow or solid, and could produce a range of toys which are tough and
9 durable, yet can incorporate special features, such as 'shining' eyes, ears, a laser
10 gun which emits 'laser' light, or a number of other accessories for toys / movie
11 theme characters.

12

13 Use can be made of the dielectric stack mirror onto these materials to produce
14 numerous effects. e.g. a car track can be designed to reveal an effect similar to
15 'shining' cat's eyes; a toy garage can have its sign illuminated; lights illuminating
16 the floor of a small swimming pool; windows which appear to have a light
17 switched on inside the room of a toy house etc.

18

19 Games which utilise the capture of sunlight, with the subsequent emission of a
20 range of visible colours can be designed.

21

22 As the peg is pushed through the sheet of light absorbing material, it comes into
23 contact with the sheet of light-emitting material, and this allows the light to pass
24 into the peg, which then becomes illuminated.

25

26 Safety.

27

28 Fibres have a certain amount of light 'leaking' out along its length. This is
29 dependant upon the refractive indices of both the doped material and the substance
30 in contact with this material, and also on the amount the material is bent. From
31 these facts, there are three techniques which can be applied to improve peoples'

1 safety in dark conditions or when poor visibility exists.

2

3 By capturing sufficient sunlight into a section of the fibre which is exposed to the
4 sun, then light will leak out gradually along that part of its length which is placed
5 within the darkened conditions. In this way, anyone can follow the illuminated
6 fibre out of the darkened room to safety. An example of such a device and the
7 principles involved, is shown in Figure 27.

8

9 The second and third techniques involve the same principles of injecting light into
10 the fibre as the one just described. However, the second technique makes use of the
11 fact that a bend in the fibre will cause an increased amount of light to leak out. This
12 may be useful where an increased amount of light is necessary in order to be seen
13 (e.g. in smoke-filled rooms). Also, the spacings between the bends can be utilised
14 to inform the people which is the quickest way out of the room (e.g. decreasing
15 spaces indicates the way out).

16

17 The third technique makes use of the substance in contact with the doped material.
18 If a substance which has a refractive index similar to the doped material is placed
19 in contact with it, then an increased quantity of light will leak out. This can both be
20 used to make that area more easily visible and also to provide information. (e.g. the
21 geometrical shape of the substance (e.g. →) can be selected to guide the person
22 from the room in the easiest manner.)

23

24 Two other methods of capturing light from outside a building and introducing it
25 into the inside are by using a sheet on the outside to collect the light and by
26 attaching fibres to the edges of the sheet, the light is coupled to the fibres, which
27 can then be fed into the inside of the building. The other method of transferring
28 light to the inside of a building is by using a longer length(s) of fibre / rod on the
29 outside and passing the fibre into the interior.

30

31 Another safety application could be as sails, or sail coating, so that the edge of the

1 sail becomes more easily visible in misty, foggy conditions, or when the light level
2 is poor.

3

4 People who go out jogging in poor conditions could also benefit from wearing an
5 outer garment which is made from, or has patches of, this material. Jogging shoes
6 could also benefit in a similar way. They would be more easily seen by motorists,
7 and so help to avoid accidents.

8

9 Cars, motorcycles and cyclists can also benefit from fitting sections of this
10 fluorescent material onto their external surfaces, so that other motorists /
11 pedestrians can see them more easily. This can take the form of a warning strip
12 which can be seen on e.g. all four sides of a car.

13

14 Airport runway illumination.

15

16 An application of light-emitting fibres / rods is that of airport runway
17 lights, where a series of these rods are placed on either side of the runway, and each
18 rod is suitably angled towards the incoming aircraft. An example of such a device
19 and the principles involved, is shown in Figure 28.

20

21 This application would be for daytime use, and the existing system of runway
22 lighting would be used during the hours of darkness.

23

24 Fashion accessories.

25

26 A range of accessories can be designed to take advantages of the materials' light-
27 emitting qualities. These include raincoats with edges that shine, clothes or cloth,
28 patches, broches, rings, jewellery, necklaces, bangles etc.

29

30 Other types of concepts include candles with a light-emitting 'flame' and
31 Christmas tree lights.

1

2 24 hour bus arrival scheduler.

3

4 This is a communication device, mounted at a bus stop, which informs potential
5 passengers when the arrival of the next bus(es) is due. It takes the form of a
6 satellite communications receiver / decoder, linked up to a display which consists
7 of a doped material which can operate even during the hours of darkness. This can
8 be achieved using material which can absorb light from street lights (from the
9 sodium D lines 589.0 and 589.6 nm) and convert it to red fluorescent light. A solar
10 panel can be used to charge a battery which provides power for the
11 communications receiver and the electronically-controlled shuttering for the
12 display. A back-up night light can be provided to enhance the visibility of the
13 display in conditions where the street lights are poor. This would also be powered
14 by the battery.

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31